



(1) Publication number:

0 596 580 A1

EUROPEAN PATENT APPLICATION

(1) Application number: 93203109.9

(i) Int. Cl.5: **D06M 13/46**, D06M 15/11

2 Date of filing: 05.11.93

(3) Priority: 05.11.92 NL 9201939

Date of publication of application: 11.05.94 Bulletin 94/19

Designated Contracting States:
BE DE ES FR GB IT NL SE

Applicant: Coöperatieve Verkoop- en Productievereniging van Aardappelmeel en Derivaten 'AVEBE' B.A. Beneden Oosterdlep 27 NL-9641 JA Veendam(NL)

(2) Inventor: Drudis Zambrano, Josep Maria Rambla del Jardi 76 E-08190 Valldoreix(ES) Inventor: Hesseling, Henderik Dr. Kopplusstraat 39 NL-9641 CG Veendam(NL)

Representative: Smulders, Theodorus A.H.J., Ir. et al
Vereenigde Octroolbureaux
Nieuwe Parklaan 97
NL-2587 BN 's-Gravenhage (NL)

(see Liquid fabric softening compositions.

The invention relates to a liquid aqueous fabric softening composition comprising a biodegradable fabric softener. In this composition a thickener is incorporated which is capable of giving the composition the desired viscosity and which moreover is highly biodegradable. According to the invention, as such thickener, gelatinized cationic starch is used, preferably in an amount between 0.1 and 5 wt.%.

This invention relates to liquid aqueous fabric softening compositions based on biodegradable cationic fabric softeners.

For more than 25 years now, fabric softeners have been used for aftertreating washed textile products. Fabric softening compositions consist of aqueous dispersions of cationic fabric softeners. Typically, these compositions further comprise a number of adjuvants, such as fatty alcohols, fatty acids, emulsifiers, aromatic substances, dyes, preservatives and electrolytes.

Fabric softening compositions are mostly added to the last rinsing water in a washing machine after the washing process. The cationic fabric softeners are adsorbed by the anionic textile fibers and lend the dried textile product the desired soft "feel" and antistatic properties. In addition, the use of fabric softening compositions has still other favorable effects on the dried textile product, such as a pleasant odor, improved ironing properties, and a higher wear resistance.

The fatty acids and/or fatty alcohols present in the fabric softening compositions have a favorable effect on the softness of the dried textile product (function as co-softeners). In addition, these compounds play a role in stabilizing the viscosity of the fabric softening compositions.

Known fabric softeners are the quaternary ammonium salts such as di-stearyl di-methyl ammonium chloride (DSDMAC) and certain imidazolinium salts, such as alkylmethyl-imidazolinium chloride. Up to about 1990, substantially exclusively fabric softeners of poor biodegradability were used.

In many countries the consumer desires to use liquid fabric softening compositions that possess a viscous texture. A viscous aqueous composition with non-biodegradable fabric softeners can be obtained by adapting the product process, by the use of suitable fatty acids or fatty alcohols and/or by the use of certain thickening agents. According to European patent specification 51.983, guar gum, certain guar gum derivatives, polyacrylamides and polyvinyl acetate are used as thickening agents in liquid fabric softening compositions. In this patent specification it is mentioned that cationic guar gum products are not suitable because flocculation of the cationic fabric softeners develops (page 2, last paragraph). The thickeners used must ensure that the viscosity of the viscous fabric softening compositions does not undesirably change during prolonged storage.

The use of non-biodegradable fabric softeners and adjuvants meets with ever increasing resistance on account of the environmental problems they cause. For that reason, biodegradable fabric softeners have in the meantime been put on the market by various manufacturers. These biodegradable fabric softeners are described *inter alia* in European patent applications 293.953 and 293.955 and in U.S. Patent 4,789,491. However, liquid fabric softening compositions comprising biodegradable fabric softeners are often insufficiently stable during storage (see European patent application 293.953, page 2, lines 26-28 and U.S. Patent 4,789,491, column 1, lines 44-48). Accordingly, there is a need for thickeners for these fabric softening compositions that are biodegradable and stabilize the viscosity of these compositions for longer periods of time.

According to U.S. Patent 4,789,491, in fabric softening compositions comprising biodegradable fabric softeners, cellulose ethers, certain synthetic polymers (polyvinyl alcohol, polycarboxy polymers) or cationic guar gum derivatives can be used as thickeners (column 12, lines 32-38). Objections to these thickeners are their high price and/or their slight biodegradability.

35

Applicant has now found that, as thickener in liquid fabric softening compositions comprising biodegradable fabric softeners, cationic starch products can be used with advantage. These cationic starches are relatively inexpensive and are biodegradable to a great extent.

The present invention accordingly relates to liquid aqueous fabric softening compositions based on biodegradable fabric softeners, with gelatinized cationic starch being present in the composition as thickening agent.

It has been found that compositions with cationic starch as thickening agent possess a surprisingly high viscosity. This means that for the production of compositions with a specified desired viscosity relatively little cationic starch is necessary.

The aqueous compositions of the invention possess a water content of preferably 60 to 97% by weight. The pH of the fabric softening composition of the invention is typically between 1 and 5 and preferably between 2 and 4. The desired pH can be set by means of acids.

Methods of producing cationic starch are described by D.B. Solarek; Cationic Starches in the book of O.B. Wurzburg (Ed), Modified Starches: Properties and Uses, CRC Press, Inc., Boca Raton, Florida, 1986, pp. 113-130. As starting material for the manufacture of the cationic starch to be used in accordance with the present invention, all types of starch can be used, such as potato starch, corn starch, wheat starch, tapioca starch, pea starch and the types of starch that have an amylopectin content of more than 95% by weight (based on solids). Prior, after or during the cationization reaction, the starch can be modified physically, chemically and/or enzymatically. The expression "cationic starch" as used herein encompasses

these additionally modified starch products. The degree of substitution (DS) of the cationic starch to be used in accordance with the invention is preferably between 0.005 and 0.5 and preferably between 0.01 and 0.2. The amount of cationic starch (solids) to be used in accordance with the invention is preferably between 0.1 and 5% by weight, and more preferably between 0.2 and 1.5% by weight, based on the weight of the liquid aqueous fabric softening composition.

The liquid aqueous fabric softening composition may further comprise various adjuvants and additives such as aromatic substances, dyes, preservatives, electrolytes, dispersing agents, emulsifiers, fatty acids, fatty acid alcohols, salts and nonionic surfactant compounds.

The cationic starch to be used in accordance with the invention is preferably first gelatinized in water, whereafter the starch solution obtained (optionally after cooling) is mixed, with stirring, with an aqueous dispersion of the biodegradable fabric softener. It is also possible to mix pregelatinized cationic starch (as dry product or after dissolution in water) with the aqueous fabric softener dispersions.

In the following examples, the Henkel product Au-48 is used as cationic biodegradable fabric softener. This product comprises 90% by weight of active material (methyl-triethanolammonium-distearate-methyl sulfate) and 10% by weight of isopropanol.

An aqueous dispersion of the fabric softener is obtained by mixing Au-16 with demineralized water and stirring the mixture for 30 minutes at 1500 rpm. The dispersion obtained is diluted to the desired fabric softener concentration by adding demineralized water.

The starch solution to be used is obtained by mixing the starch product into demineralized water through stirring and heating the mixture obtained, with stirring, at 90 to 95 °C for 30 minutes. Then the starch solution obtained is cooled to 20 °C. This starch solution is diluted to the desired starch concentration by adding water.

The liquid fabric softening compositions are obtained by mixing the aqueous dispersion of the fabric softener with the starch solution, in such amounts that the compositions prepared contain the desired amounts of fabric softener and starch product. If desired, additives, as preservatives and aromatic substances, such as are allowed according to the relative regulations, can be incorporated into the fabric softening compositions.

The fabric softening compositions tested in Examples 1, 2 and 3 have the following composition:

cationic fabric softener Au-46
starch product
water and additives

4 wt.%
0.4-1.5 wt.%
balance up to 100 wt.%

The starch products used in the examples are the following:

Detete steveh	antiva natata atavah
Potato starch	- native potato starch
Amylofax 00 1)	- cationic potato starch with DS 0.017
Amylofax PW 1)	- cationic potato starch with DS 0.035
Amylofax HS 1)	- cationic potato starch with DS 0.048
Retamyl AP 2)	- urea potato starch phosphate
Farazym 3)	- potato starch acetate with DS 0.027
Perfectamyl AC 3)	- potato starch acetate with DS 0.07
Solvitose Xo 3)	- hydroxypropyl potato starch with DS 0.07
Perfectamyl P ₁₀ X ²⁾	- distarch phosphate

1) cationic starch

2) starch with introduced anionic substituents

3) starch with introduced nonionic substituents

The viscosities (in mPa.s) specified in the following examples were determined with a Brookfield viscosimeter, type RVT, at 20 rpm, spindle 2 and 20 °C.

Example 1

Various types of starch product were used as thickening agents in liquid fabric softening compositions. Table 1 shows the influence of the type of starch product on the viscosity and the stability (during storage at 20 °C) of the liquid fabric softening compositions.

3

50

45

30

Table 1

Viscosities in mPa.s at 20 °C starch product wt.% starch storage time in days (at 20 °C) Amylofax PW 1.5 Retamyl AP 1.5 Farazym 1.5 PerfectamyI AC 1.5 Solvitose Xo 1.5 PerfectamyI P10X 1.5

Table 1 shows that cationic starch lends a much higher viscosity to the fabric softening compositions in comparison with other types of starch with incorporated anionic or nonionic substituents. It further appears that this viscosity remains highly stable during storage of the composition.

Example 2

In this example the influence of the amount of cationic starch on the viscosity of the fabric softening composition is determined.

Table 2

Viscosities in mPa.s at 20 °C wt.% starch starch product storage time in days (at 20 °C) Control 0.0 Potato starch 8.0 Amylofax 00 0.4 Amylofax 00 8.0 Amylofax 00 1.2 0.4 Amylofax PW Amylofax PW 0.8 Amylofax PW 1.2 0.4 Amylofax HS Amylofax HS 8.0 1.2 Amylofax HS

It appears from Table 2 that cationic potato starch lends liquid fabric softening compositions a higher viscosity than does native potato starch (at equal concentrations). It further appears that the viscosity of the compositions increases with increasing starch concentration and remains properly stable in time.

Example 3

In this example the influence of the storage temperature on the viscosity of the fabric softening compositions is determined.

Table 3

Viscosities in mPa.s at 20 °C wt.% starch storage time in days (at 37 °C) starch product 28 84 14 Amylofax 00 1.0 320 390 395 390 300 260 Amylofax PW 1.0 480 470 410 370 305 225 280 Amylofax HS 1.0 350 350 330 315 240 220 230 220 Perfectamyl AC 1.0 195 195 150 Solvitose Xo 1.0 140 145 128 110 88 64

It appears from Table 3 that even at a storage temperature of 37 °C the cationic starches lend liquid fabric softening compositions a higher viscosity than do the starch products with incorporated nonionic substituents.

Example 4

It is evident from this example that cationic starch lends high-concentration fabric softening compositions (12 wt.% fabric softener) a high and stable viscosity.

Table 4

25

30

20

5

10

Viscosities in mPa.s at 20 ° C							
starch product	starch product wt.% starch storage time in days (at 20 °C))		
		0	2	14	35	98	
Amylofax PW Control	0.5 0.0	2000 180	2050 220	2350 265	2350 295	2450 340	

35 Claims

- A liquid aqueous fabric softening composition based on a cationic biodegradable fabric softener, characterized in that this composition comprises gelatinized cationic starch as thickening agent.
- 40 2. A fabric softening composition according to claim 1, characterized in that between 0.1 and 5 wt.% of cationic starch (solids) is present in the composition (calculated on the liquid composition).
 - 3. A fabric softening composition according to claim 2, characterized in that between 0.2 and 1.5 wt.% of cationic starch (solids) is present in the composition (calculated on the liquid composition).
 - 4. A fabric softening composition according to claims 1-3, characterized in that the degree of substitution of the cationic starch is between 0.005 and 0.5.
- A fabric softening composition according to claim 4, characterized in that the degree of substitution of the cationic starch is between 0.01 and 0.2.
 - A fabric softening composition according to claims 1-5, characterized in that the pH of the composition is between 1 and 5.
- 55 7. A fabric softening composition according to claim 6, characterized in that the pH of the composition is between 2 and 4.

8. A fabric softening composition according to claims 1-7, characterized in that the composition comprises

		60-97 wt.% of water.
5	9.	Use of gelatinized cationic starch as a means of obtaining a stable viscous aqueous fabric softening composition of good degradability, based on a cationic biodegradable fabric softener.
10		
15		
20		
25		
30		
35		
40		
45		
50		

55

Category	Citation of document with indication, where appropriate, of relevant passages			devant claim	CLASSIFICATION OF THE APPLICATION (Int.CL5)	
X	US-A-4 179 382 (A.L * the whole documer		1-9)	D06M13/46 D06M15/11	
X	FR-A-2 440 433 (UNI * the whole documer					
x		A-0 044 003 (HENKEL) he whole document *		2,8		
x	Class A96, AN 85-08	s Ltd., London, GB;	1			
x	* page 1 - page 8 *	PROCTER & GAMBLE CO.) - page 18, line 13;	1-5	5,8,9	TECHNICAL FIELDS SEARCHED (Int.Cl.5)	
x	DE-A-29 25 859 (HEM * claims *	VKEL)		8,8	C11D D06M	
X	US-A-4 421 566 (M.J. * the whole documer	1 566 (M.J. HASULY ET AL.) le document *		2,8		
X	FR-A-2 353 633 (THE PROCTER & GAMBLE CO.) * page 2, line 5 - page 13, line 4; claims *			5,8		
A	 EP-A-O 458 599 (UNILEVER) * claims 1,6,9,10 *		1-3	3,6-8		
D,A	US-A-4 789 491 (N.J. CHANG ET AL.) * the whole document *		1,6	5-9		
	The present search report has	been drawn up for all claims	_			
	Place of search	Date of completion of the search	,	¢	Examiner	
	THE HAGUE	31 January 199			betsoglou, A	
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background			locumen date d in the l for othe	in the application		